

### The Spectrum Characteristic of Hydrogen Bonds\*

It has been observed that in certain substances containing hydroxyl hydrogen the relatively narrow and intense absorption bands which ordinarily are characteristic of the O-H group appear to be absent. Since in these cases it appears very probable that the hydroxyl hydrogen is involved in the formation of the type of linkage known as the "hydrogen bond" it has been suggested that the absence of the bands may be taken as a criterion for the presence of such bonds.<sup>1</sup> On the other hand the O-H fundamental band appears strongly in a number of substances containing hydroxyl groups in which the hydrogens are supposed to be engaged in linkages which Bernal and Megaw prefer, in this case, to call "hydroxyl bonds."<sup>2</sup> These substances include ice and a number of minerals examined by Coblenz.<sup>3</sup> These observations have left the situation somewhat unclear since they leave the question open as to whether the O-H absorption in the cases first mentioned has merely shifted to some new region where it has not been observed, or whether it has really disappeared. If the latter were true there would appear to be a considerable difference between the hydrogen linkages in the two cases.

In order to throw light on the question we have investigated the absorption in the photographic infrared of a number of substances which are generally accepted to contain hydrogen linkages of one sort or another. In the vapor of acetic acid, under conditions in which the material is largely dissociated into single molecules, the narrow O-H band at  $\lambda 9750$  was found to be intense, but as association was increased by lowering the temperature or increasing the pressure it became progressively weaker. Indeed the intensity of this band was found to be a measure of the concentration of single molecules and it was found possible to follow the association equilibrium photometrically with results in agreement with MacDougall's vapor density measurements.<sup>4</sup>

In dilute solutions of methyl alcohol in carbon tetrachloride and of ethyl alcohol in carbon disulfide the sharp O-H band was observed at  $\lambda 9577$  and  $\lambda 9658$ , respectively, but with increasing concentration it rapidly diminished in intensity. However, in all three cases as the narrow O-H band disappeared it was replaced by new absorption regions as was observed by Errera and Mollet<sup>5</sup> in the region of the fundamental band in ethyl alcohol solutions. These new regions appear to be characteristic of an hydroxyl group in which the hydrogen is involved in a hydrogen bond.

We have observed similar features in the spectra of liquid ethyl acetoacetate, methyl and ethyl alcohol, sulfuric, formic and acetic acid, and of carbon tetrachloride solutions of the last two and of trichloroacetic acid. In all cases there appears a broad absorption region extending from about  $\lambda 10900$  to  $\lambda 9700$ , with a maximum around  $\lambda 10100$ . In some cases the band appears to have some structure which is best resolved in the carbon tetrachloride solutions. In the organic acids there are at least two components while in the alcohols there are four or five which simultaneously make their appearance as the

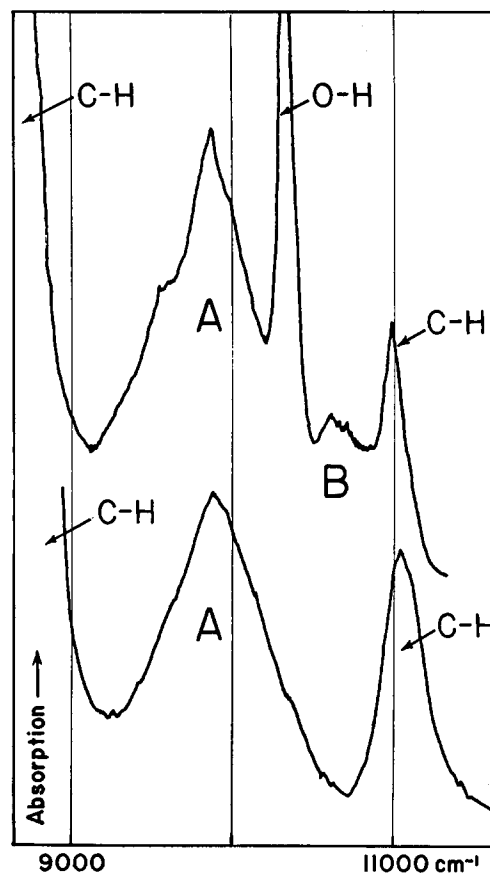


FIG. 1. Microphotometer curves showing the shift and broadening of the O-H band accompanying hydrogen bond formation. The upper curve, of a solution of ethyl alcohol in carbon disulfide at moderate concentration (10 percent by volume) shows the two bands A and B characteristic of associated alcohol molecules as well as the sharp O-H band of the single molecules. The lower curve, of ethyl acetoacetate, shows only one broad O-H band.

solutions are increased in concentration. For this reason we believe they are not due to polymers of different sorts but to the complexity of the smallest polymers which are present in appreciable concentration.

In the alcohols we have observed an additional absorption region on the short wave side of  $\lambda 9600$ . This is of moderate width and relatively very weak. It is definitely absent in sulfuric acid, and in the other cases its presence is doubtful.

At first sight it appears that the O-H absorption is weakened as the hydrogen becomes involved in a hydrogen bond, but this is not at all the case and the appearance is due to the spreading out of the absorption region to at least ten times its original extent.

Since the disappearance of the narrow O-H bands as criterion for the presence of hydrogen bonds has largely been applied to aromatic compounds we have attempted observations on such substances. Unfortunately in these cases the C-H bands extend well into the region where we have found the characteristic spectrum described above and it has been difficult to draw any certain conclusions.

However, from the similarity of the results in the other cases it appears reasonable to conclude that there is a rather definite spectrum characteristic of the O-H group of which the hydrogen atom is engaged in a hydrogen bond. In the substances studied these bonds appear to be quite similar and the distinction between hydrogen and hydroxyl bonds appears to be somewhat artificial. From the rather moderate shift in the O-H frequency in the formation of the bond it appears that the binding of the hydrogen to the oxygen atom to which it originally belonged has not been greatly affected and consequently that the internuclear distance is probably only slightly larger than the normal O-H separation.

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<sup>1</sup> Hilbert, Wulf, Hendricks and Liddel, *J. Am. Chem. Soc.* **58**, 548 (1936).

<sup>2</sup> Bernal and Megaw, *Proc. Roy. Soc. London*, **A151**, 384 (1935).

<sup>3</sup> W. W. Coblenz, *Investigations of Infra-Red Spectra* (Carnegie Institution, 1906).

<sup>4</sup> F. H. MacDougall, *J. Am. Chem. Soc.* **58**, 2585 (1936).

<sup>5</sup> Errera and Mollet, *Nature* **138**, 882 (1936).

#### Concerning the *Q* Branch and Analysis of the Hydrogen Sulfide Band at 10100A

Following an unsuccessful attempt to obtain more than seventeen lines in the hydrogen sulfide band at 10100A, Carvin<sup>1</sup> has recently questioned the validity of the previous measurement and analysis of this band.<sup>2</sup>

Carvin cites specifically the four strongest lines of the *Q* branch and one line of the *P* branch as definitely missing. Four of these lines were measured on all fourteen plates of the earlier work, while the fifth was measured on twelve of the fourteen plates. These lines were still observable, though greatly broadened, at pressures as high as 4 atmospheres.

An attempt is made here to reproduce portions of two of the best plates of the series upon which the original report and analysis were based. Enlargements of the original plates on process film were contact-printed on process film, and the latter printed on contrast paper. Practically all the lines reported as of intensity 2 or more are visible on these prints, as well as many of intensity 1, but considerable detail is lost in the halftone reproduction (Fig. 1). Since the original plates (Eastman type 1Q) were used beyond the region in which they are most suitable, they show a marked gradation in intensity which renders quite difficult their reproduction with high contrast. In addition, the slight irregularities in intensity resulting from unevenness of the supersensitization in ammonia are so enhanced as to offset a considerable portion of the gain in clarity afforded by the contrast-reproduction process.

The author wishes also to make use of this opportunity to present the evidence which convinces him that the analysis is unquestionably correct. In Fig. 2(b) are shown the observed lines which gave the clue to the analysis, and on the same scale the calculated positions of the transitions assigned to these lines. (The calculated values are from an unpublished work of Crawford and Cross in which this band is treated by the correct centrifugal distortion theory developed by Wilson.<sup>3</sup> The assignments are the same as in

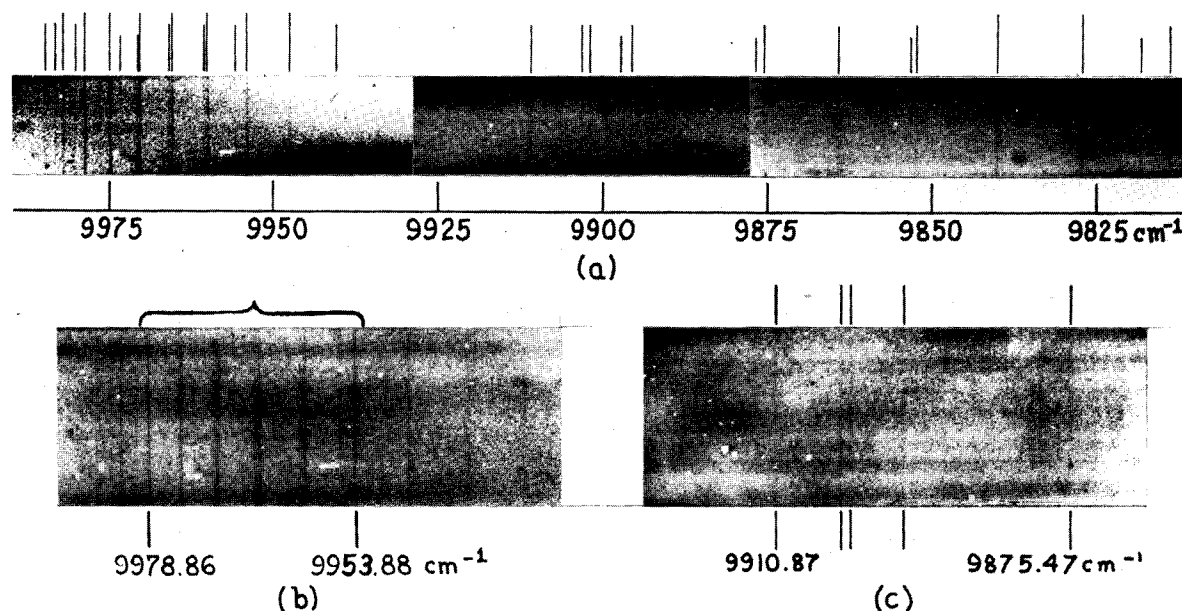


FIG. 1. Absorption band of hydrogen sulfide at 10100A. (a) shows the *R*, *Q* and *P* branches (the latter to 9812  $\text{cm}^{-1}$  only) together with the lines given in the original report as having intensities of 5, 4, or 3. (b) shows the *R* branch, with the brace indicating the group of lines whose satisfactory assignment confirms the correctness of the original analysis. (c) shows the region of the band center, containing the lines of the *Q* branch from which the original analysis was primarily derived. Special attention is called to the lines reported by Carvin to be "definitely missing."